# Highly Lewis Acidic Bifunctional Organoboranes

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Chelating Lewis acids have not been developed to the same degree as multidentate Lewis bases. Nonetheless, such compounds have attracted interest due to their potential for the enhanced activation of basic substrates and the selective binding of anions. Organodiboryl compounds form a class of bidentate Lewis acids which have a long, but relatively underdeveloped history. Many examples exist where donor groups on boron serve to stabilize the Lewis acid centers. More recently, advances in the chemistry of diboryls with highly Lewis acidic boron centers substituted with perfluoroaryl groups have been made. In particular, compounds of general formula $(F_5C_6)_2B$–linker–$B(C_6F_5)_2$ have been prepared and their chemistry examined. In this Microreview, we survey the classes of bifunctional boron Lewis acids known, including their synthesis, properties and anion binding chemistry. Particular emphasis is placed on the role these Lewis acids play in olefin polymerization catalyst generation from simple metallocene precursors.

## Introduction

Despite the early recognition of the potential utility of multidentate Lewis acids, development in this area has lagged far behind the extensive chemistry associated with chelating Lewis bases.[1] The reasons for this stem partly from the synthetic difficulties associated with the preparation of molecules with multiple Lewis acid sites, which in turn is related to the high reactivity of these species. These factors can be partially ameliorated by the incorporation of groups capable of stabilizing the Lewis acid centers through either strong σ-donation or π-bonding. In fact, most of the examples of group 13 element based bidentate Lewis acids in the literature make use of this strategy, at least to some degree.[2] Since one of the primary reasons for investigating these molecules is to achieve a greater degree of substrate activation, reducing the Lewis acid strength of each center to some extent defeats the purpose of their preparation.

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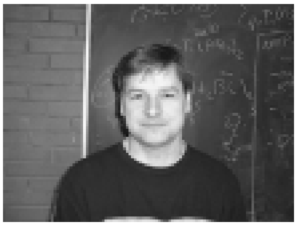

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**MICROREVIEWS:** This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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Nonetheless, impressive advances have been made in the synthesis and use of aluminum,[3] mercury,[4] tin[5] and titanium[6] based bifunctional Lewis acids, which show that two Lewis acid centers can act in concert to effect increased substrate activation or greater reaction selectivity.

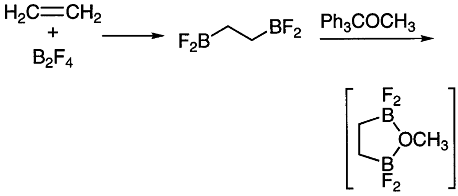
It has been recognized for many years that the pentafluorophenyl group is an excellent replacement for a halogen ligand in boron Lewis acids.[7] For example, the $C_6F_5$ group has similar σ-electron-withdrawing powers to those of Cl and F but the $B{-}C_{aryl}$ bonds in $B(C_6F_5)_3$ are more kinetically inert in the presence of protic agents.[8] Therefore, although $B(C_6F_5)_3$ loses some Lewis acidity due to the front strain associated with the bulkier $C_6F_5$ substituents,[9] it is more easily handled and generally as effective as $BX_3$ Lewis acids in terms of strength,[9,10] without the problems inherent with reactive B−X bonds.

A natural extension of the rise to prominence of this monodentate Lewis acid[11] is a recent surge of activity in the preparation of multifunctional boranes (and other group 13 elements) in which the boron centers are of comparable Lewis acid strength to the highly Lewis acidic monofunctional boranes $RB(C_6F_5)_2$ (R = alkyl, alkenyl, aryl, $C_6F_5$). Although interest in these compounds arises primarily because of their role in the activation of neutral organometallic complexes for olefin polymerization processes, such diboryl targets are also of interest in the arenas of organic synthesis,[12] anion recognition[13] and the formation of new polymeric materials.[14] Furthermore, two strong, proximal Lewis acid centers have the potential to act as "superelectrophiles".[15]

After setting the stage with a brief history of strongly Lewis acidic bifunctional boranes, we will discuss recent developments in this area, along with specific related examples. The bidentate Lewis acids will be grouped by the number of atoms in the bridge connecting them; diboranes with no atom in the bridge, i.e. diborane(4) compounds $R_2B{-}BR_2$, will not be considered here. Although it has been shown that such compounds can bind two Lewis bases,[16] their potential as chelating acids is negligible. These compounds do, however, have potential as reagents for the preparation of chelating organodiboryl Lewis acids, and this chemistry has to some extent been reviewed elsewhere.[2b]

## History of Highly Lewis Acidic Organodiboryl Compounds

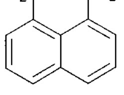
The first important study aimed at investigating the chelating properties of a bidentate Lewis acid was conducted by Shriver and Biallas in the late 1960's.[17] The reactions of a bidentate version of the quintessential boron-based Lewis acid ($BF_3$) with simple Lewis bases and anions were investigated. They found that $F_2BCH_2CH_2BF_2$, prepared by mixing ethylene and $B_2F_4$ at low temperature,[18] did not readily chelate neutral bases, but that anions such as $OMe^-$ were bound by both borane centers. Given the high reactivity of the B−F bonds in this bidentate Lewis acid, incorporation of the anions required weakly basic reagents such as $Ph_3COMe$ [Equation (1)] to avoid metathetical replacement of the boron fluorides. Amido bridging groups were also incorporated as their tropylium salts.



(1)

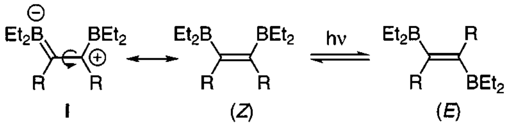
This compound was the first diboryl derivative with strongly Lewis acidic boron centers, but despite these early and very promising successes, research in bifunctional borane Lewis acid chemistry appears to have been sporadic for close to two decades subsequent to these publications. Although $F_2BCH_2CH_2BF_2$ is a relatively simple looking compound on paper, looks can be deceiving; undoubtedly the difficulties in preparing and handling this compound, in particular the synthesis of the precursor $B_2F_4$, have something to do with its disappearance from the literature since the seminal studies of Shriver and Biallas. Perhaps the disappointing performance of this acid in binding neutral Lewis bases, of most interest to organic chemists, also contributed to its demise.

A series of papers by Katz in the mid 1980′s describing the use of a 1,8-bis(dimethylboryl)naphthalene (**1a**) as a "hydride sponge" was the next major study on the applications of a chelating diboryl.[19] Other anions, such as $F^-$ and $OH^-$ were also bound effectively by this compound. Katz showed quantitatively, through competitive binding studies involving monodentate analogs, that two boron centers are better than one for binding these anions. To bind chloride, however, the more Lewis acidic chloro derivative **1b** was required.[20] This compound was prepared via a transmetallation reaction between an organomercury precursor and $BCl_3$ in refluxing toluene in 86% yield. Although sensitive B−Cl functions tended to limit the usefulness of this species, the other side of the coin is that these bonds may be readily functionalized. To this end, Reilly and Oh have recently used the Katz compound to prepare chiral bidentate Lewis acids in situ via derivatization of the chloro boranes with chiral ligands such as (*R*)-BINOL, for use in Diels−Alder couplings.[21] However, it is unclear whether the two borane centers cooperate in activating the substrates in this system.



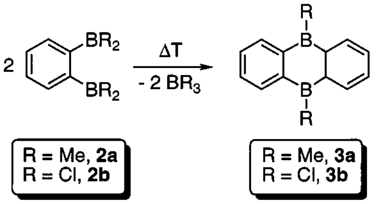
R = Me, **1a**
R = Cl, **1b**

Two final types of organodiboryls we wish to mention highlight some of the chemistry which might be expected to feature prominently in more strongly Lewis acidic organodiboryls. The groups of Köster and Wrackmeyer[22] and Siebert[23] have both published widely on 1,2-diboryls bridged by alkenyl fragments. A variety of methods for the synthesis of these compounds has been developed, including addition of $X_2B-BX_2$ or $BI_3$ across the C≡C bond of internal alkynes. Like the Katz compounds discussed above, the *cis*-alkenyl diboryls are capable of binding various first row halogen equivalents when the $BR_2$ fragments are *cis* disposed about the C=C double bond. In Köster's work, the R substituent was for the most part the relatively electron rich, but metathetically inert, ethyl group, and incorporation of the anions $X^-$ can be accomplished by treatment of the diboryls with various potassium salts.[22a] The free *cis*-1,2-diboryls, however, were found to be susceptible to photoisomerization about the double bond, producing equilibrium mixtures of the (*Z*) and (*E*) isomers [Equation (2)].[22b] The barrier to double bond isomerization is decreased because the empty p orbital on the boryl centers can overlap with the C=C π-bond and lower the bond order of the double bond through resonance structures akin to **I**, allowing for more facile isomerization. This phenomenon might be expected to be more prevalent in diboryls with stronger Lewis acidic boron centers, such as the pentafluorphenyl-substituted family considered here. However, it should be noted that only the (*Z*) isomer is capable of chelating anions and the foundational work of Katz[19] has shown that these anions are thermodynamically favored over their monodentate analogs.



(2)

One way to avoid this problem is to incorporate backbones which cannot isomerize. Kaufmann et al. were the first to prepare the 1,2 phenylene bridged tetrachlorodiboryl species via metathesis from aryl silane[24] or stannane[25] precursors. This work brought to light the thermal instability of some of these compounds towards condensation reactions which eliminate $BR_3$. For example, heating $1,2\text{-}C_6H_4(BR_2)_2$ (**2a**, R = Me; **2b**, R = Cl) leads to loss of $BR_3$ and production of the 9,10-diboraanthracene compounds **3** [Equation (3)]. As will be seen, these 9,10-diboraanthracene derivatives are interesting Lewis acids in their own right, but in terms of the synthetic targets **2**, their generation is an undesirable side reaction which must be overcome. Eisch and his group have extended the scope of boron−tin exchange reactions substantially in an effort to produce organodiboryls with a variety of backbones, including −C≡C−, RC=CR and $1,2\text{-}C_6H_4$,[26] and note that this thermally induced condensation reaction is a feature of the chemistry of diboryls with backbones other than $1,2\text{-}C_6H_4$.

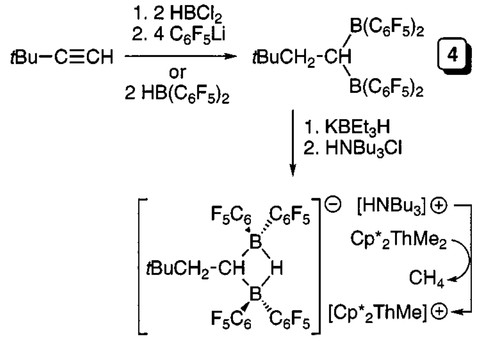


(3)

Development of the chemistry of chelating organoboranes, while not extensive, does have a rich history, as the above discussion briefly illustrates. Nevertheless, until very recently diboryl Lewis acids incorporating perfluoroaryl groups have not been explored. Given the considerable advantages of the $C_6F_5$ group, such compounds have great potential as anion receptors, olefin polymerization initiators and as synthons for the preparation of new weakly coordinating anions. The performance of a given diboryl in each of these areas will be influenced strongly by the nature of the bridge employed to link the two Lewis acid centers. In addition to its effects on the Lewis acid strength of the borane centers, the backbone will dictate the bite angle of the chelate and the separation of the two borane centers and hence the nature of the anions which will be most strongly bound. We now consider the recent progress in perfluoraryl-substituted diboryl Lewis acids, grouped by the number of atoms in the bridge connecting the two boron centers.

## $B(Ar_F)_2$ Units Bridged by One Atom

The first report of a bidentate borane incorporating $C_6F_5$ groups came from the Marks group in 1994.[27] The borane $t\text{BuCH}_2\text{CH}[B(C_6F_5)_2]_2$ (**4**) was prepared by the metathetical route shown in Scheme 1.



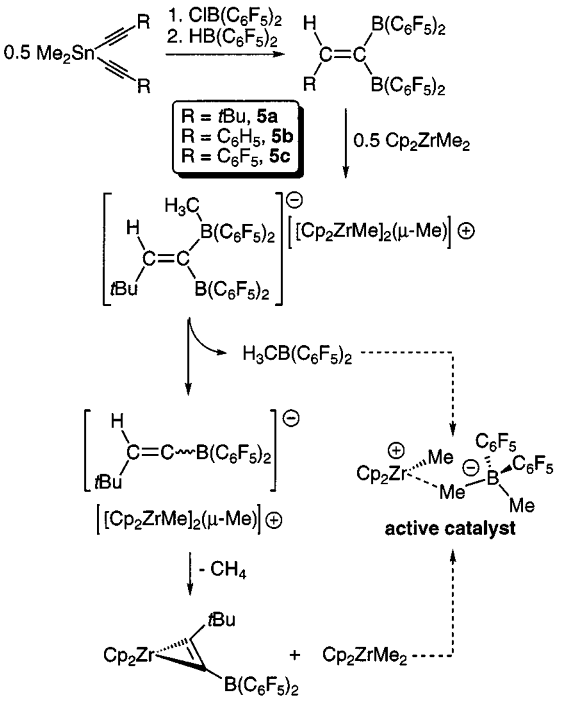
Scheme 1

We have also shown that this borane, along with other examples, can be prepared via dihydroboration of terminal alkynes using the hydroboration reagent $HB(C_6F_5)_2$.[28] The motivation for this work was to employ these boranes as precursors to weakly coordinating anions in homogeneous olefin polymerization catalysts. To this end, Marks developed a route for converting the free 1,1-diboryl to the $[HNBu_3]^+$ salt of the μ-hydridodiborate which, in combination with the thoracene catalyst precursor $Cp_2{}^*Th(CH_3)_2$ formed stable ion pairs capable of polymerizing ethylene, or hydrogenating 1-hexene in the presence of dihydrogen. It was envisioned that diborate anions from this family of boranes would more effectively delocalize the negative charge, and thus reduce the coulombic interaction between cation and anion, leading to more active catalysts. This expectation was borne out in slightly increased activities for ethylene polymerization and 1-hexene hydrogenation compared to cationic permethylthoracene catalysts incorporating more conventional $[H_3CB(C_6F_5)_3]^-$ or $[B(C_6F_5)_4]^-$ counteranions.[27] The lack of $H^-$ transfer back to the thorium center also suggested that the hydride is effectively chelated by the two borane centers, another potential advantage of bidentate Lewis acids for this particular application.

Although reactions of the free bifunctional borane $t\text{Bu}CH_2CH[B(C_6F_5)_2]_2$ with dialkyl metallocenes were not reported in detail, the need to convert into an anionic hydridodiborate prior to use suggests that the free borane is not very effective as an activator by itself. In our brief exploration of the chemistry of these diboryl alkanes, we found evidence that facile retrohydroboration, yielding (*E*)-$t\text{Bu}CH{=}CHB(C_6F_5)_2$ and $HB(C_6F_5)_2$, has a dominating influence on the reactivity of these species towards Lewis bases. As an example, when **4** was treated with one equivalent of acetone, the small amounts of $HB(C_6F_5)_2$ present in solutions of $t\text{Bu}CH_2CH[B(C_6F_5)_2]_2$ reacted rapidly with the acetone to yield $i\text{PrOB}(C_6F_5)_2$, leaving (*E*)-$t\text{Bu}CH{=}CHB(C_6F_5)_2$;[29] the reaction is pulled in this direction by the facile retrohydroboration equilibrium present in the system. Given the high reactivity of metallocenes toward $HB(C_6F_5)_2$,[30] this represents a potential problem for the use of this type of diboryl for direct activation of neutral organometallic alkyls which must be circumvented by prior formation of a diborate. Even if methide abstraction was favored, our study of a closely related system suggests that other problems can arise.

As an alternative to diborate formation, retrohydroboration can be precluded by incorporating unsaturation in the backbone; hence, we prepared the 1,1-diboryl alkenes[31] $RCH{=}CH[B(C_6F_5)_2]_2$ (R = *t*Bu, **5a**; $C_6H_5$, **5b**; $C_6F_5$, **5c**) using tin−boron exchange/hydroboration procedures as shown in Scheme 2.[32]

In combination with $Cp_2ZrMe_2$, these 1,1-diboryls form reasonably active ethylene polymerization catalysts, although ion-pair stability was only moderate given the propensity of the methide anions formed to eject $H_3CB(C_6F_5)_2$[30a] (Scheme 2). Spectroscopic studies on the ion-pairs formed from **5a** and $Cp_2ZrMe_2$, in the absence of ethylene, show that the abstracted methide ligand is associated with the boron center *trans* to the *t*Bu group, the most sterically accessible Lewis acid in this crowded system. Sterically undemanding Lewis bases also coordinate exclusively to this boron center in reactions with **5a**.[29] Loss of $H_3CB(C_6F_5)_2$ from this anion is presumably facilitated by the stability of the boryl-substituted vinyl anion,[33] which rapidly couples with the cationic zirconocene center. Separate experiments showed that the boryl alkyne zirconocene derivative is not capable of polymerizing ethylene under the reaction conditions and thus represents a catalytic dead-end. The methyl borane, however, is itself a strong Lewis acid capable of partial abstraction of methide from $Cp_2ZrMe_2$ and, indeed, careful analysis of the data from ethylene polymerization experiments led us to conclude that the active catalyst in these systems is in fact the ion pair derived from $H_3CB(C_6F_5)_2$ and $Cp_2ZrMe_2$! Clearly, Marks' strategy of preparing stable anions from groups which are readily chelated[27] (i.e. $H^-$ and not $CH_3^-$) prior to incorporation into a catalyst system was appropriate for these systems.



Scheme 2

Two other one-atom bridged diboryl Lewis acids have been prepared and characterized. Green and co-workers incorporated an HN bridge,[34] while the μ-oxo species $[(C_6F_5)_2B]_2(\mu\text{-O})$ (affectionately known as "BOB") has been prepared by both our lab and that of Collins[35] by controlled hydrolysis of either $HB(C_6F_5)_2$ or $ClB(C_6F_5)_2$. A priori, a reduction in the Lewis acid strength of the boron centers in both of these molecules may be expected due to π-donation from the bridging atom; geometrical parameters from the X-ray structures of $(Me_3Si)_2NB(C_6F_5)_2$[34] and "BOB" indicate that B−N and B−O π-bonding is significant. Interestingly, however, the B−O−B moiety in BOB is not linear; bending occurs so that one boron center is able to accept donation of a lone pair from one of the *ortho* fluorine groups of the other borane.[35] The binding of anions or Lewis bases to these compounds has not been explored as yet.

Selectivities for binding various anions $X^-$ by bidentate Lewis acids will obviously be profoundly influenced by the bite angle provided by the backbone linker. In these one-atom bridged diboryls, the bite angle can be parameterized

Table 1. Selected geometrical parameters for 1,1-diboryl Lewis Acids

| Compound | B···B (Å) | B−atom−B (°) |
|---|---|---|
| $[(C_6F_5)_2B]_2(O)$ | | 154.05(12) |
| $[(C_6F_5)_2B]_2(NH)$ | 2.53[a] | 134.0[a] |
| $t\mathrm{BuCH_2CH[B(C_6F_5)_2]_2}$ | 2.63[a] | 116.1[a] |
| $\{t\mathrm{BuCH_2CH[B(C_6F_5)_2]_2}\}(\mu\text{-H})^-$ | 1.94 | 75.0[b] |
| $t\mathrm{BuCH{=}CH[B(C_6F_5)_2]_2}$ | 2.673(8) | 118.7(4) |
| $\mathrm{PhCH{=}CH[B(C_6F_5)_2]_2}$ | 2.731(2) | 123.22(13) |
| $(C_6F_5)CH{=}CH[B(C_6F_5)_2]_2$ | 2.721(6) | 121.7(4) |

[a] Estimated values based on semi-empirical AM1 geometry optimization calculation. – [b] B−C−B.

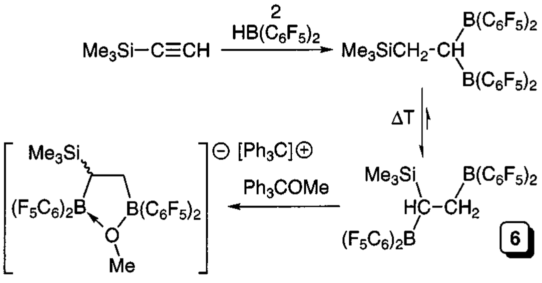
by the B−atom−B angle and the B···B distance; Table 1 collates these data for the compounds discussed in this section.

The values for the B−atom−B angles and interboron distances in $[(C_6F_5)_2B]_2(NH)$ and $t\mathrm{BuCH_2CH[B(C_6F_5)_2]_2}$ were obtained from a semi-empirical AM1 geometry optimization.[36] These calculated geometries around the central bridging atom are somewhat larger than the ideals of 120°and 109.5°, probably a consequence of the steric bulk of the bis-pentafluorophenylboryl substituents. Nonetheless, there is a high degree of flexibility in the saturated carbon backbone as demonstrated by the experimentally determined geometrical parameters found for the hydridodiborate anion. Although the chelation of halide anions by $t\mathrm{BuCH_2CH[B(C_6F_5)_2]_2}$ is covered in the patent pertaining to Marks' work,[37] not much has been reported so far concerning the anion binding selectivities of this type of diboryl Lewis acid. The flexibility inherent in the system suggests it should bind larger anions than hydride.

In modifying the backbone to an alkenyl fragment, the bite angle of the chelate is necessarily affected since the bridging carbon is now sp$^2$ hybridized. Although the experimental values for B−C−B in the 1,1-diboryl alkenes **5a−c** are not much larger than the calculated value for the free, saturated analog, there should be markedly less flexibility than that associated with the unsaturated system. In particular, the variation possible in the B···B separation might be expected to be smaller for these diboryls. Indeed, treatment of **5a** with $\mathrm{KEt_3BH}$ indicated that hydride addition occurred, although pure material was not isolated and it was unclear if the hydride moiety was bound by both boron centers. Bromide, on the other hand, was not complexed at all when **5a** was treated with PPNBr, indicating perhaps that $\mathrm{Br^-}$ (ionic radius = 1.82Å) is too large to fit into the chelate region of this type of diboryl. These preliminary results suggest that one-carbon bridged diboryls will not strongly bind larger anions and thus may be moderately hydride specific. However, more extensive investigations will be necessary to delineate the binding characteristics of this family of diboryls in more detail.

## $\mathrm{B(Ar_F)_2}$ Units Bridged by Two Atoms

The pioneering work of Shriver,[17] Köster,[22] Siebert,[23] and Kaufmann[24,25] described above provides obvious choices for a two-carbon linker for highly Lewis acidic, chelating organodiboryls: saturated alkyl, *cis*-alkenyl, and 1,2-phenylene. As the foregoing discussion has highlighted, saturated alkyl backbones are generally problematic due to the facility of retrohydroboration reactions. We have found one exception, however, and that is the 1,2-diboryl alkane formed upon double hydroboration of $\mathrm{Me_3SiC{\equiv}CH}$ (Scheme 3).[28a]



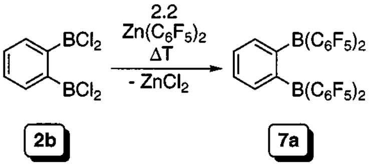
Scheme 3

Initially, a mixture of the 1,1 and 1,2 substituted isomers is observed, but upon heating gently for a couple of hours, complete conversion into the thermodynamic 1,2 species **6** is observed. This isomer is favored due to a ground state β-silicon effect which is energetically appreciable in these highly electrophilic boranes.[38] Perhaps this effect also contributes to the observation that this particular saturated diboryl derivative is less prone to the retrohydroboration complication found for **4**.

Compound **6** is not a particularly effective olefin polymerization co-catalyst on its own: stoichiometric reactions with $[\mathrm{Cp_2ZrMe_2}]$ show that rapid $C_6F_5$ transfer back to the zirconium center from the putative $[\mathbf{6}{\cdot}\mathrm{Me}]^-$ anion occurs in solution. We have found this to be a common decomposition pathway for anions of this general form, i.e. $[\mathrm{RR'B(C_6F_5)_2}]^-$, perhaps a reflection of the greater nucleophilicity of this more electron-rich borate anion. Deployment of Marks' strategy, i.e., converting **6** into an anion with an activating countercation, yields more encouraging results. For example, **6** reacts smoothly with trityl methyl ether ($\mathrm{Ph_3COMe}$) to give an OMe anion (Scheme 3) as an orange solid.[39] The precise details of its structure are unknown, but two signals at δ = 41.4 and 5.7 in the $^{11}$B NMR spectrum and a complex (but clean) $^{19}$F NMR spectrum containing signals for four chemically different $C_6F_5$ groups point to an unsymmetrical structure as depicted in the scheme. The metallocene activating properties of **6** and its derivatives are currently under investigation.

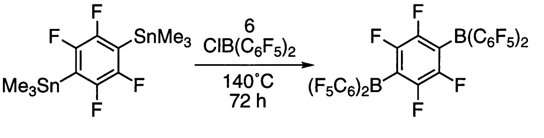
Of more interest as target diboryls are those with unsaturated *cis*-alkenyl- or 1,2-phenylene-type backbones, since these are more rigid and the effectiveness of electron-withdrawing backbones would be heightened due to the conjugation possible. Our efforts towards the 1,2 alkenyl objectives, in addition to inherent synthetic challenges, have to some extent been beset by the photoisomerization problem identified in Köster's studies.[22b] We have, however, recently made significant progress towards the 1,2-phenylene-bridged systems, preparing both the unsubstituted and perfluorinated members of this family of compounds.[40]

The proteo substituted 1,2-phenylene bridged derivative **7a** was straightforwardly prepared from Kaufmann's tetrachlorodiborane 1,2-$C_6H_4(BCl_2)_2$ (**2b**)[24,25,41] and $[Zn(C_6F_5)_2]$[42] as a $C_6F_5$ transfer agent[43] [Equation (4)]. The intraboron region of this molecule is quite sterically hindered and the Lewis acidity of the two boron centers is dampened by virtue of the nonfluorinated backbone substituent;[44] consequently the anion binding chemistry of this species is somewhat limited. Nevertheless, the B···B separation in this molecule is 3.263(3)Å and the anions $SCN^-$, $Cl^-$, $Br^-$, $OMe^-$ were found to interact with both boron centers in a bridging binding mode. $^{19}F$ NMR spectroscopic studies on the interaction of **7a** with these anions revealed only weak coordination and, in some cases, an equilibrating mixture of reactants and products could be observed. In all cases examined, the weak binding of these anions precluded isolation of the products from solution. Neutral donor molecules such as THF did not appear to bind appreciably in solution, attesting to the steric demands of this Lewis acid.



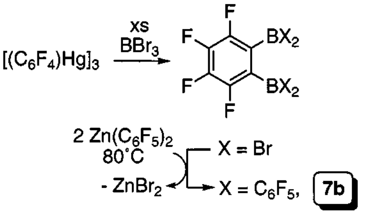
(4)

Of course, a system with a fully fluorinated phenylene backbone would be of more interest due to the increased Lewis acidity of the boron centers and the incorporation of more robust $B-C_{backbone}$ bonds. As is common, the more desirable target molecule is considerably more difficult to prepare! Our first attempts involved boron−tin exchanges between the trimethyltin-substituted perfluoroaryl precursor 1,2-$C_6F_4(SnMe_3)_2$[45] and $ClB(C_6F_5)_2$.[46] With two equivalents of the chloroborane, we found the major products to be 1,2-$C_6F_4(SnClMe_2)_2$ and $H_3CB(C_6F_5)_2$,[30a] the products of chloro−methyl exchange. We did not push this route any further, not wanting to sacrifice too much $ClB(C_6F_5)_2$, but Marks et al. have shown in a recently published patent[47] that the closely related 1,4-substituted diboryl Lewis acid can be prepared by this method [Equation (5)] using six equivalents of $ClB(C_6F_5)_2$.



(5)

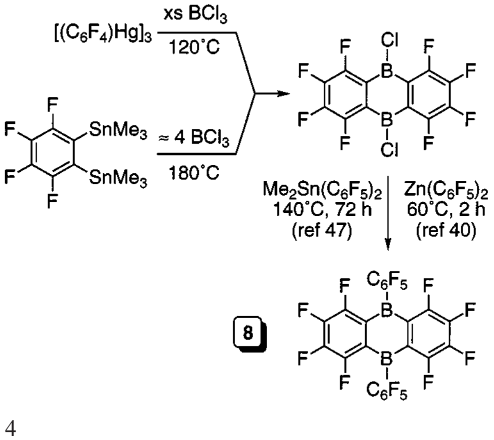
Eventually, we settled on the mercury trimer $[(C_6F_4)Hg]_3$[48] as a "$C_6F_4$" synthon for the preparation of **7b**. Reaction of $[(C_6F_4)Hg]_3$ with $BBr_3$ gives 1,2-$C_6F_4(BBr_2)_2$ which must be converted relatively quickly to the fully perfluoroaryl-substituted system using $[Zn(C_6F_5)_2]$ due to its thermal instability [Equation (6)]. The first two $C_6F_5$ groups are incorporated at ambient temperatures, but the third and fourth require heating to install successfully. The solid state structure of **7b** reveals a B···B separation of 3.138(2)Å, large enough to incorporate at least first row element anions comfortably; indeed, this compound has a rich anion binding chemistry associated with it (vide infra).



(6)

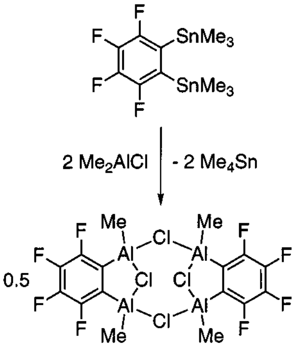
While **7b** is quite thermally stable, the tetrahalides are susceptible to the condensation reaction observed by Kaufmann and Eisch, producing 9,10-diboraanthracene derivatives. Both our group[40] and the Marks group[47] have made this observation independently (Scheme 4). In our laboratory, we noted that reaction of the mercury trimer with $BCl_3$ instead of $BBr_3$ leads directly to $[1,2\text{-}C_6F_4B(Cl)]_2$, which in turn could be converted into the pentafluorophenyl-substituted derivative **8** by treatment with $[Zn(C_6F_5)_2]$. Similarly, Marks' patent discloses a preparation of **8** which involves treatment of the organotin precursor 1,2-$C_6F_4(SnMe_3)_2$ with excess $BCl_3$ at high temperatures. In both procedures the high temperatures necessary to effect the transmetallations preclude isolation of 1,2-$C_6F_4(BCl_2)_2$, which condenses rapidly under these conditions. It is also possible that condensation occurs from the product of one transmetallation step, i.e. 1,2-$[C_6F_4(BCl_2)(SnMe_3)]$.[47b] To convert into **8**, Marks uses the organotin $C_6F_5$ transfer agent $[(C_6F_5)_2SnMe_2,]$,[49] which serves as well as the zinc reagent.

The entropically favorable condensation reaction is driven by the high temperatures used in the transmetallation reactions involving $BCl_3$ and the organomercury or -tin precursors. The greater facility of the transmetallation reaction between $[(C_6F_4)Hg]_3$ and $BBr_3$ (allowing for lower reaction temperatures) is part of the reason this reaction leads to the desired tetrabromide 1,2-$C_6F_4(BBr_2)_2$. Qualitatively, the condensation of 1,2-$C_6F_4(BCl_2)_2$ appears to occur under milder conditions. In



Scheme 4

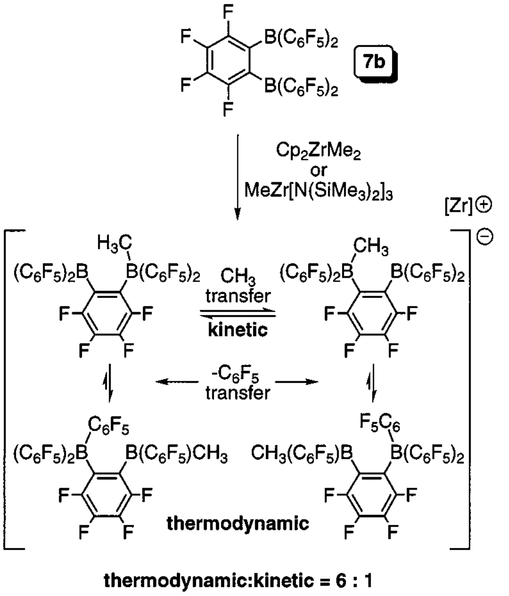
a closely related study recently reported by Gabbaï et al.,[50] the reaction of 1,2-$C_6F_4(SnMe_3)_2$ with $Me_2AlCl$ at room temperature produces the dimer shown in Equation (7).[51] Possibly, this intriguing dimer provides a model for how the elimination of $BCl_3$ from 1,2-$C_6F_4(BCl_2)_2$ occurs. The Gabbaï group has also reported related derivatives of indium.[52]



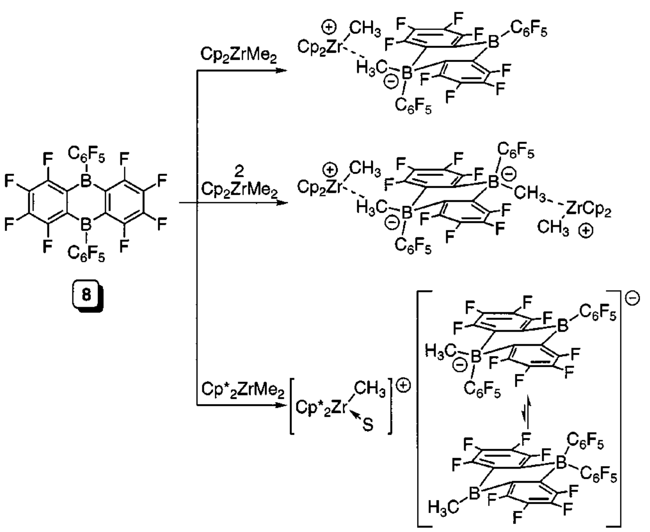
(7)

Both perfluorinated diboryl- **(7b)**[53] and diboraanthracene **(8)**[47,53] activate $[Cp_2ZrMe_2]$ to form active ethylene polymerization catalysts. In the case of the former activator, the anion formed upon methide abstraction from the metallocene is an equilibrating mixture of two species (Scheme 5). In other words, the poorly bridging methide anion is not chelated by the two Lewis acid sites. Nonetheless, detailed dynamic $^{19}F$ NMR spectroscopy experiments indicate that exchange of both $CH_3$ and $C_6F_5$ between the boron centers is occurring. In particular, the pattern of cross-peaks observed in the resonances for the backbone fluorine atoms can only be accounted for by invoking transfer of both groups, although, qualitatively, transfer of $CH_3$ is slower than transfer of the aryl group. In this system, the major anion is the one containing the tetraaryl borate moiety; this is apparent from the integrals observed for key resonances in the $^{19}F$ NMR spectrum of the mixture, and from an X-ray analysis of this major species using the tris-amido cation $\{Zr[N(SiMe_3)_2]_3\}^+$ to engender crystallinity. Thus, the other boron center consists of a neutral borane containing a B−$CH_3$ moiety. We postulate that this species is able to complex $[Cp_2ZrMe]^+$ in much the same way as $AlMe_3$,[54] accounting at least in part for the slightly lower activities observed for catalysts derived from **7b** and $[Cp_2ZrMe_2]$ in comparison to the parent $B(C_6F_5)_3$/$[Cp_2ZrMe_2]$ system.[53]

The bifunctional borane **7b** does not appear to abstract two methyl groups when treated with excess $[Cp_2ZrMe_2]$. In contrast, diboraanthracene **(8)** will react with one or two equivalents of $[Cp_2ZrMe_2]$ to form the ion pairs shown in Scheme 6. Marks has shown that the borane centers in **8** are strongly Lewis acidic,[47b][47c] relative to $B(C_6F_5)_3$, and they appear to act essentially independently to activate two equivalents of metallocene. It is likely that the ion pair formed from **8** and one equivalent of $[Cp_2ZrMe_2]$ is stabilized by close contact between the ions via the abstracted methide bridging group.[55] We have shown in unpublished work that when a more separated ion pair is formed by employing a bulkier metallocene such as $[Cp^*_2ZrMe_2]$, the anion formed from **8** and $CH_3^-$ is susceptible to $C_6F_5$ migration as shown in the reaction scheme. As was observed for the related compound **7b**, the anion formed following methide abstraction from the metallocene is a mixture of two species. The major species in solution is the anticipated kinetic product containing the aryl−methyl−borate moiety and a neutral arylborane center. This species is readily identified in the $^{19}F$ NMR spectrum by comparison with the ion pair formed from $[Cp_2ZrMe_2]$. The minor species possesses a trigonal B−$CH_3$ center and a diarylborate functionality. This anion is $C_{2v}$ symmetric, giving rise to a simplified $^{19}F$ NMR spectrum and comprises ca. 16% of the product mixture. The facility with which $C_6F_5$ migration occurs in this system is probably related to the magnitude of ion pair association. Our experiments show that **8** is comparable to $B(C_6F_5)_3$ as a co-catalyst for ethylene polymerization using $[Cp_2ZrMe_2]$,[53] and the Dow/North-



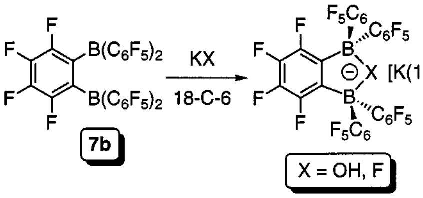
Scheme 5



Scheme 6

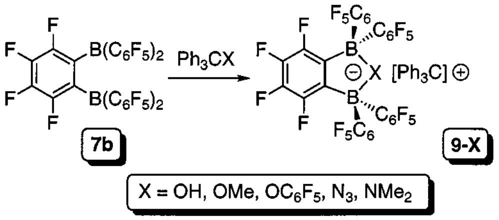
western Patent claims significantly higher performance (an order of magnitude) using **8** vs. $B(C_6F_5)_3$ in conjunction with a titanium based CGC catalyst.[47]

Since the methide anion of **7b** exhibits the behavior described above, we have sought to convert it into a weakly coordinating anion with countercations capable of activating neutral organometallic precursors. The $B\cdots B$ separation of 3.138(2)Å suggests that small first row anions may be incorporated. Indeed, solutions of **7b** in dichloromethane soak up one equivalent of KF or KOH rapidly; addition of 18-C-6 allows for isolation of these potassium salts [Equation (8)].[40] Spectroscopic data indicate that both $F^-$ and $OH^-$ are held between the two boron centers in a symmetrical fashion, although a crystal structure of the former does reveal that the fluoride is tilted out of the B−C−C−B plane.[56] A dynamic process in which this μ-F wags in and out of this plane could account for the observed temperature dependence of the chemical shift for this fluorine atom in the $^{19}$F NMR spectrum.[40]

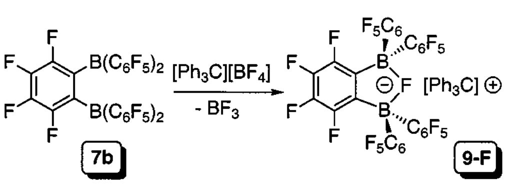


(8)

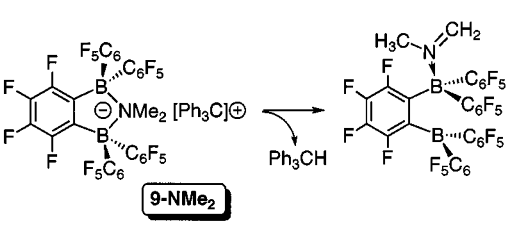
Anions with cations more amenable to olefin polymerization applications can be straightforwardly prepared by reacting **7b** with various trityl derivatives $Ph_3C-X$ (X = OH, OMe,[57] $OC_6F_5$,[57] $N_3$, $NMe_2$); the fluoride derivative is generated upon treatment of **7b** with $[Ph_3C]^+[BF_4]^-$ [Equations (9) and (10)]. These reactions are generally rapid and quantitative by NMR spectroscopy and, with the exception of X = $NMe_2$, the resulting trityl salts, **9−X**, are stable in solution and the solid state. In **9−NMe$_2$**, the trityl cation abstracts $H^-$ from a methyl group of the bridging amido to form an imine adduct of **7b** in which only one of the borane Lewis acids interacts with $H_2C{=}NMe$ [Equation (11)]. Interestingly, this type of behavior is not in evidence for **9−OMe**; even heating at moderate temperatures for several hours did not lead to formation of any $Ph_3CH$, although other decomposition processes did occur. Preparation of compounds **9−NR$_2$** without abstractable β-hydrogens using trityl amine reagents failed due to the greater steric bulk of these species. However, we are optimistic that $NR_2$ groups can be employed in conjunction with ammonium salts as cations allowing for study of this family of anions.



(9)

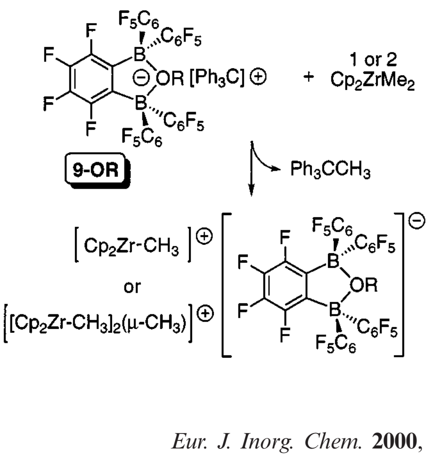


(10)



(11)

The bite angles (B−O−B) found for **9−OMe** [117.72(12)°] and **9−OC$_6$F$_5$** [115.4(5)°], which are close to ideal for sp$^2$ hybridized oxygen, suggest that the alkoxides are bound quite tightly by **7b**. Of the stable trityl salts **9**, the μ-alkoxides are highly effective as weakly coordinating anions in metallocenium chemistry, particularly **9−OC$_6$F$_5$**.[57] Thus, the monomeric and dimeric metallocenium cations derived from $[Cp_2ZrMe_2]$ and one or one half equivalents of **9−OR**, respectively, were found to be stable in bromobenzene solution for several hours (Scheme 7).[57] Little is known about the details of the ion−ion contact in these compounds as efforts to crystallize these species have thus far failed, and solution studies in more noncoordinating solvents such as toluene are plagued by the formation of liquid clathrates. Clearly, the $OC_6F_5$-derived anion is less coordinating towards $[Cp_2ZrMe]^+$ than the OMe species, as evidenced by the lower stability of the monomeric ion pair derived from **9−OC$_6$F$_5$** in the absence of monomer, and its greater polymerization activity in the presence of monomer.[57] It should be noted, however, that both anions are remarkably robust. Decomposition processes at room temperature appear to involve only the cation, since the $^{19}$F NMR spectra of the anions remain unchanged over time. Upon heating, some $C_6F_5$ transfer to zirconium is observed, but no evidence of OR transfer is discernable. Furthermore, **7b** rapidly abstracts $OCH_3^-$ from $[Cp_2Zr(OCH_3)_2]$; although the cation in the resulting species is not very stable, the $^{19}$F and $^{11}$B NMR spectra show clean formation of the μ-$OCH_3$ anion. Taken together, these observations suggest that these μ-OR anions of **7b** are ther-



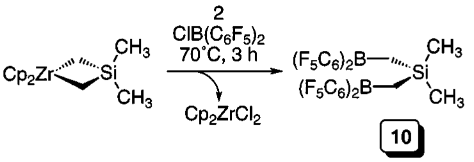
Scheme 7

modynamically stable in the presence of metallocenium cations.

This contrasts with the anions **9−F** and **9−N$_3$**, which rapidly transfer the X$^-$ anion to zirconium when the cationic center is formed upon removal of a methide by the trityl abstractor.[58] In these systems, clean reactions are observed when the trityl salts are treated with two equivalents of [Cp$_2$ZrMe$_2$], and the chemistry which ensues is depicted in Scheme 8 for the case of **9−F**. The first equivalent of metallocene undergoes alkide abstraction but the ion pair formed forthwith is not observed. Rather, a new ion pair in which the anion is the methide anion of **7b** described above, is the only product seen. The cation is a μ-F dimer ($^{19}$F NMR resonance at $\delta = -90.4$[59]) formed from [Cp$_2$ZrMe]$^+$ and the neutral methyl fluoride [Cp$_2$Zr(Me)F] produced in the first step. Similar species appear to be formed in the reaction involving **9−N$_3$**, as evidenced by the signature $^{19}$F NMR spectrum for [**7b**·Me]$^-$;[53] the cationic portion of this ion pair has not been rigorously characterized, although the $^1$H NMR spectra are consistent with a dimeric μ-N$_3$ metallocenium ion.

## B(Ar$_F$)$_2$ Units Bridged by Three or More Atoms

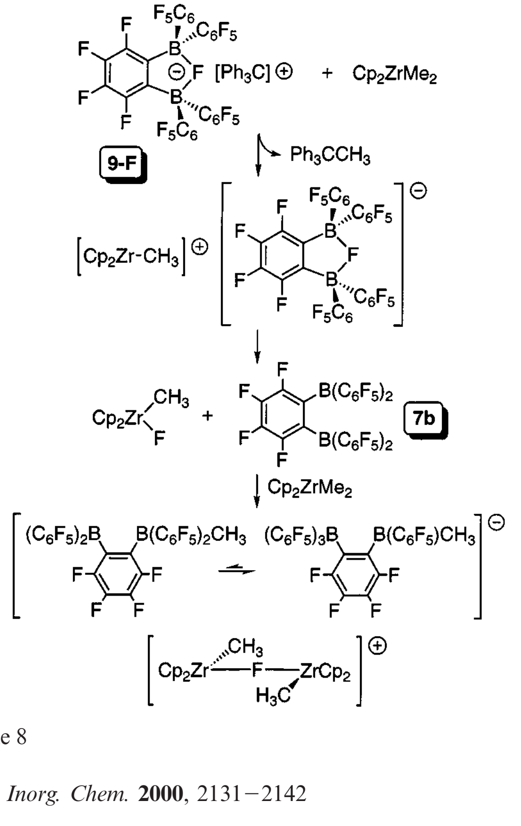
In theory, longer bridges should provide diboryl derivatives capable of binding larger anions. To this end, we prepared the three-atom bridged system **10**[60] shown in Equation (12). We felt the lack of β-hydrogens would make this an effective backbone and, furthermore, the compound is trivially synthesized using Petersen's zirconasilacyclobutane[61] and ClB(C$_6$F$_5$)$_2$. The 1,3-diboryl compound **10** is a relatively weak Lewis acid, binding acetophenone only at low temperature and failing to react with trityl methyl ether at room temperature. It is possible that the Lewis acidity of the borane centers is tempered somewhat by the β-silicon atom in the backbone (see above[38]), but other factors must be involved since **6** reacts smoothly with Ph$_3$COMe (see Scheme 3 above). The reactions of **10** with [Cp$_2$ZrMe$_2$] are complex, characterized by the rapid production of [Cp$_2$Zr(C$_6$F$_5$)Me]. The ultimate fate of the anion is unknown and, given the compound's properties, we have not pursued its chemistry further.



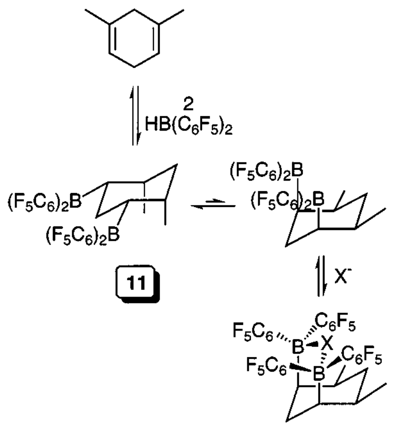
(12)

Green and co-workers have synthesised a 1,3 diborylcyclohexyl compound **11**, by hydroborating 1,3-dimethylcyclohexa-1,4-diene with two equivalents of HB(C$_6$F$_5$)$_2$ as shown in Scheme 9.[62] Addition of the borane is highly regiospecific, and the favored conformation places the two boryl groups in the equatorial sites. Binding studies with suitable anions suggest that the molecule can change conformation such that the two borane centers occupy axial sites, tethered via chelation. However, because of reversible anion binding, there are sufficient quantities of the unbound diboryl Lewis acid present. Due to the reversibility of the initial hydroboration, reactions involving reagents which react with HB(C$_6$F$_5$)$_2$ deplete the system of **11**.

Green and co-workers have also reported the preparation and reactivity of difunctional boronous esters with either tetrahydro or tetrafluorocatecholate bridges [Equation (13)].[62] Reaction of the catechols with ClB(C$_6$F$_5$)$_2$ produces **12a** and **12b** in good yield. Both compounds are weaker Lewis acids than most of the preceding C$_6$F$_5$-substituted diboryls discussed by virtue of the π donating oxygen on the boron centers. In the presence of neutral Lewis bases, both borons of **12b** act independently. Thus, with one equivalent of a Lewis base (such as acetone or THF) one boron center binds whilst the other remains three coordinate, but if the base is present in excess, both coordinate

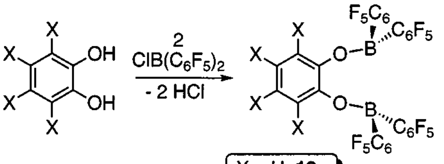


Scheme 8



Scheme 9

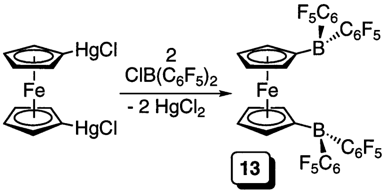
weakly. In the presence of dimethyl zirconocene, compound **12b** rapidly transfers catecholate to zirconium, leaving two equivalents of $MeB(C_6F_5)_2$, suggesting that the thermodynamic stability of this type of ion pair relative to neutral products is poor.



X = H, **12a**
X = F, **12b**

(13)

A final example from our group utilizes a ferrocenyl backbone to connect two $B(C_6F_5)_2$ moieties. Although we have not explored the anion binding capabilities of this system to a great degree, others have found that 1,1′-substituted diboryl metallocenes bind hydroxide anion effectively.[63] The diborylferrocene compound **13** is straightforwardly prepared from a transmetallation reaction using the well-known 1,1′-bis(chloromercuri)ferrocene[64] [Equation (14)].[65] Direct borylation with $HB(C_6F_5)_2$ is possible but does not proceed selectively to the 1,1′ substituted system and requires harsh conditions. Competitive binding studies using ketones indicates that **13** is a poorer Lewis acid than a comparative species, namely $C_6H_5B(C_6F_5)_2$.



**13**

(14)

## Conclusions and Future Prospects

Marks′ initial report in 1994[27] was the beginning of an intense period of research into diboryl compounds of general formula $(F_5C_6)_2B{-}\text{linker}{-}B(C_6F_5)_2$. Our work in this area has taught us some lessons regarding what the "linker" should be in order to be an effective bidentate Lewis acid. Specifically, the best performing compounds contain backbones which are both unsaturated (no β-hydrogens) and electron-withdrawing (preferably perfluorinated). The former feature prevents the facile retrohydroboration of $HB(C_6F_5)_2$, while the latter engenders more inert $B{-}C_{backbone}$ bonds (i.e., more stable backbones) and more Lewis acidic boron centers. This is an important point, since the greater steric bulk of these diboryls tends to dampen the Lewis acidity of the individual boron centers. Furthermore, a perfluorinated backbone prevents rapid back transfer of $C_6F_5$ groups to metallocenium cations in olefin polymerization applications by lowering the nucleophilicity of the borate formed upon methide abstraction.

With these features in mind, there is much opportunity for further development in this area. New backbones, different aryl groups on boron and more extensive and imaginative anion binding chemistry are areas we continue to explore. The development of chiral versions of these diboryls[66] is also of interest, both for stereospecific olefin polymerization and applications to organic synthesis.[67] While several of the compounds described are relatively poor activators themselves, their power lies in their use as synthons for the preparation of very weakly coordinating anions with other, stronger countercation activators ($Ph_3C^+$, $HNR_3^+$).[27,57] The effectiveness of these anions lies in the diboryl′s ability to sequester small anions through strong chelation and steric protection in the bidentate pocket of the bifunctional borane binding site.

## Acknowledgments

WEP wishes to express his gratitude to all the talented co-workers cited for the work described herein, in particular Dr. Katrin Köhler, whose work laid the foundation for our efforts in this area. Also, the important contributions of collaborators Scott Collins (Waterloo) for polymerization studies, William Clegg (Newcastle) for X-ray crystallography and Todd Marder (Durham) are acknowledged. The authors also thank Prof. Malcolm Green (Oxford) for allowing inclusion of unpublished work from his group and Prof. Tobin Marks for sharing results prior to publication. Financial support for our work was provided by the Natural Sciences and Engineering Council of Canada's Strategic Projects program (STR192869) and the EPSRC (UK) . WEP thanks the Alfred P. Sloan Foundation for a Research Fellowship (1996−00).

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